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FISH, WILDLIFE, AND ESTUARIES

Dieldrin and Heptachlor Residues in Dead Gray Bats, Franklin County, Missouri—1976 Versus 1977

Donald R. Clark, Jr.,[1] Richard K. LaVal,[2] and Alexander J. Krynitsky[1]

ABSTRACT

Lethal dieldrin concentrations were found in the brains of dead gray bats (Myotis grisescens) *collected during 1976 and 1977 beneath a maternity roost in a Missouri cave. In addition, residues of heptachlor epoxide, oxychlordane,* cis-*chlordane, and* trans-*nonachlor increased significantly in both brains and carcasses of bats collected during 1977. These increases appear to reflect a switch by local farmers from aldrin, dieldrin's parent compound, to heptachlor for the control of cutworms. They also constitute an additional threat to this colony of this endangered bat species.*

Introduction

Lethal concentrations of dieldrin were found in brains of gray bats (*Myotis grisescens*) found dead beneath maternity roosts in two Missouri caves in late June and early July 1976 (*2*). The apparent source of the dieldrin was its parent compound, aldrin, which had been applied to cornfields to control cutworms (larvae of several moth species of the family Noctuidae). Heptachlor and toxaphene are being recommended as substitutes for aldrin in Missouri (*3*). On July 8, 1977, LaVal found 74 dead gray bats when one of the two colonies was revisited; the other colony was not revisited at this time. In the present study, authors compare the organochlorine residues found in the 1977 sample of dead bats with those found in the 1976 sample from the same cave.

Materials and Methods

The cave is located in Franklin County, Missouri. Because its precise location is confidential, it will be referred to by its number, 048, assigned by the Fish and Wildlife Service, U.S. Department of the Interior. A brief description of cave 048 has been published (*2*). All gray bats found dead in 1976 were juveniles. The 1977 sample contained 23 juveniles and 51 adults; of these, four juveniles and four adults showed no signs of decomposition and, therefore, were analyzed. Bats were recovered under authority of the Federal Endangered Species Permit PRT–8–31–C.

By the same procedures as used in 1976, the dead bats collected in 1977 were frozen, shipped to the Patuxent Wildlife Research Center, and dissected into brain and carcass components as described previously (*1*). Each brain and carcass was analyzed for *p,p′*-DDT, *p,p′*-TDE, *p,p′*-DDE, dieldrin, heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, endrin, hexachlorobenzene (HCB), toxaphene, mirex, and polychlorinated biphenyls (PCB). The recovered PCB resembled Aroclor 1260. Hexane extracts of samples were cleaned by Florisil column chromatography, and the eluate containing the pesticides and PCBs was fractionated by SilicAr column chromatography (*4*). Four fractions were collected to facilitate partitioning of endrin and dieldrin in a separate fraction. Analyses were performed on a Hewlett-Packard Model 5753 gas-liquid chromatograph as described by Prouty et al. (*5*).

Residues in 15 percent of the samples were confirmed by gas chromatography-mass spectrometry. Average percentage recoveries from spiked bald eagle (*Haliaeetus leucocephalus*) tissues were: DDE, 107; TDE, 100; DDT, 107; dieldrin, 100; heptachlor epoxide, 93; oxychlordane, 91; *cis*-chlordane, 100; *trans*-nonachlor, 100; endrin, 85; HCB, 78; mirex, 66; and PCB, 120 percent. Residue data were not adjusted on the basis of these recoveries.

Lipid levels were determined from weights of dried hexane extracts of carcasses (*4*). The lower limit of

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[2] Missouri Department of Conservation, Fish and Wildlife Research Center, Columbia, Mo. 65201.

sensitivity for residues in carcasses was 0.1 ppm pesticides and 0.5 ppm PCB; in brains, it was 0.5 ppm pesticides and 2.5 ppm PCB. Additional details of the analytical procedure are given by Clark et al. (*2*).

Geometric means are given for residues because the data were positively skewed. Residue levels reported as not detected (ND) were entered as zeros. Significance levels are: one asterisk, $0.05>P>0.01$; two asterisks, $0.01>P>0.001$; and three asterisks, $P<0.001$. For compounds which were not detected in the majority of samples for either year, comparisons between years (Table 1) were based on frequencies of occurrence rather than mean concentrations.

Dieldrin levels in the brains of all eight bats in the 1977 sample were within the lethal range as identified previously (*2*). However, among the 12 bats collected during 1976, the brains or carcasses of only ten contained lethal dieldrin levels, and dieldrin levels in the brains of two of the ten were undetermined because of laboratory errors (*2*). Therefore, the present study compares all 1977 dieldrin levels in eight brains and carcasses with just the 1976 lethal dieldrin levels found in eight brains and 10 carcasses.

Results

RESIDUES VERSUS LIPIDS IN CARCASSES

Initial examination of the residue and lipid data for carcasses indicated that the residue levels of most compounds were positively related to the amount of fat in the bat. To quantify the relationships, regressions were calculated between ppm wet weight (fresh weight) of residue and percentage fat in the carcass for the eight compounds found in the majority of samples. Results for dieldrin (1976, $r = 0.858^{**}$; 1977, $r = 0.953^{***}$) and heptachlor epoxide (1976, $r = 0.788^{**}$; 1977, $r = 0.924^{**}$) are illustrated in Figure 1. Among the six other compounds, only *trans*-nonachlor had significant regressions for both years (1976, $r = 0.645^{*}$; 1977, $r = 0.744^{*}$). Four compounds showed a significant regression only for 1977: *cis*-nonachlor ($r = 0.773^{*}$); oxychlordane ($r = 0.799^{*}$); *cis*-chlordane ($r = 0.724^{*}$); and DDE ($r = 0.729^{*}$). PCB showed no significant relationship for either year.

To account for this variation due to fat level, authors expressed residues as ppm lipid weight rather than as ppm wet weight (Table 1). Organochlorine residues in brains are unaffected by this problem, and are compared as ppm wet weight (Table 1).

TABLE. 1. *Organochlorine residues and fat levels in gray bats found dead in cave 048, Franklin County, Missouri, in 1976 and 1977* [1]

Compound	Brains, ppm Wet Weight			Carcasses, ppm Lipid Weight		
	1976	1977	t or χ^2	1976	1977	t or χ^2
Dieldrin						
Geometric mean	7.5	8.6	0.909	650	867	1.596
Range	5.0–10	4.6–13		239–1050	560–1182	
Heptachlor epoxide						
Geometric mean	0.10	2.4	4.759***	59	257	13.123***
Range	ND–1.5	0.85–3.7		36–86	204–375	
Oxychlordane						
Frequency or geometric mean	2 of 12	5 of 8	4.432*	31	68	3.577**
Range	ND–1.4	ND–2.3		16–70	21–167	
cis-Nonachlor						
Frequency or geometric mean	1 of 12	5 of 8	6.706**	36	63	2.605*
Range	ND–0.86	ND–1.0		15–70	42–108	
trans-Nonachlor						
Frequency or geometric mean	0 of 12	7 of 8	16.154***	7.6	159	4.901***
Range	ND	ND–2.1		ND–45	91–252	
cis-Nonachlor						
Geometric mean	ND	ND	—	1.5	24	4.456**
Range	—	—		ND–11	14–38	
K chlordane						
Frequency	0 of 12	1 of 8	1.579	0 of 12	7 of 8	15.772***
Range	ND	ND–0.84		ND	ND–25	
PCB (Aroclor 1260)						
Frequency or geometric mean	0 of 12	4 of 8	7.500**	163	295	2.077
Range	ND	ND–9.3		71–425	86–1000	
DDE						
Frequency or geometric mean	6 of 12	2 of 8	1.250	38	44	0.450
Range	ND–4.9	ND–1.7		13–80	6.4–160	
DDT						
Geometric mean	ND	ND	—	0.41	2.2	1.644
Range	—	—		ND–9.1	ND–19	
% Fat						
Mean	—	—	—	6.38	3.92	2.010
Range	—	—		2.21–10.83	0.96–7.88	

NOTE: ND = not detected. Significance levels are indicated as follows: * = $0.05 > P > 0.01$; ** = $0.01 > P > 0.001$; and *** = $P < 0.001$.
[1] Twelve bats were analyzed in 1976 but, for dieldrin, only the eight brains containing lethal levels and the 10 carcasses containing lethal levels are compared. For all other compounds, $n = 12$ bats. For 1977, $n = 8$ bats.

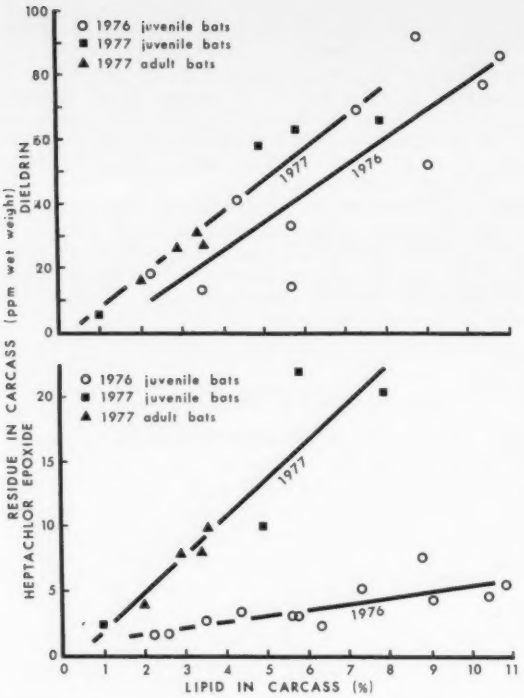

FIGURE 1. *Dieldrin and heptachlor epoxide in carcasses of gray bats in relation to lipid levels: 1976 versus 1977*

Lipid levels averaged higher in 1976, but the difference was not significant (Table 1).

RESIDUE CHANGES BETWEEN 1976 AND 1977

Between 1976 and 1977, heptachlor epoxide, oxychlordane, *cis*-chlordane, and *trans*-nonachlor increased significantly in mean concentration or frequency of occurrence in both brains and carcasses; *cis*-nonachlor and K chlordane increased significantly in carcasses; and PCB occurred significantly more often in brains of 1977 bats than in brains of 1976 bats (Table 1).

Results of covariance analyses for heptachlor epoxide (Fig. 1) and *trans*-nonachlor were similar; 1976 and 1977 regressions differed significantly in both slope and elevation (heptachlor epoxide, slope $F = 38.63^{***}$, elevation $F = 27.83^{***}$; *trans*-nonachlor, slope $F = 6.61^{*}$, elevation $F = 41.25^{***}$). However, there were no such differences for dieldrin (Fig. 1). Plots for oxychlordane and *cis*-nonachlor showed relationships between 1976 and 1977 that resembled the one for heptachlor epoxide (Fig. 1). However, statistical comparisons between years were not possible because the 1976 regressions for oxychlordane and *cis*-nonachlor were not statistically significant.

Discussion

The data in Table 1 and Figure 1 suggest that heptachlor is being substituted for aldrin over the feeding area of the gray bats from this colony, because heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, and K chlordane are either present in or degrade from commercial heptachlor. Similarly, the residues could result from the use of commercial chlordane; authors assume heptachlor was used because Missouri Farm Management Specialists are recommending it as a substitute for aldrin (*3*). Two factors indicate local usage. First, other analytical data from this laboratory show residues of heptachlor epoxide, *cis*-chlordane, and dieldrin in the insect prey of these bats at known feeding localities adjacent to crop fields. Second, the cave where the bats spend the winter is in Shannon County, Missouri, which is approximately 75 percent forested and has almost no row crop agriculture.

The data in Table 1 and Figure 1 also indicate that dieldrin levels have not declined. Authors cannot explain the apparent increase in PCB levels.

In cowbirds (*Molothrus ater*), red-winged blackbirds (*Agelaius phoeniceus*), grackles (*Quiscalus quiscula*), and starlings (*Sturnus vulgaris*) that were fed commercial chlordane, brain levels of heptachlor epoxide and oxychlordane appeared to be the primary cause of death (*6*). Heptachlor epoxide residues in brains of birds that died after chlordane dosage ranged from 3.4 to 8.3 ppm whereas residues in brains of survivors ranged from 0.87 to 3.2 ppm (*6*). Among the 1977 bats (Table 1), only one contained heptachlor epoxide residues (3.7 ppm) that reached or exceeded 3.4 ppm. Oxychlordane residues in brains of birds that died after chlordane dosage ranged from 1.1 to 5.0 ppm, and residues in brains of survivors ranged from 0.18 to 1.7 ppm. (*6*). Among the 1977 bats (Table 1), one contained 2.3 ppm oxychlordane but all others had 0.76 ppm or less. In sum, authors doubt that heptachlor residues contributed to the deaths of these 1977 bats because heptachlor concentrations were generally below lethal levels, whereas 1977 dieldrin levels in brains were lethal. However, if the heptachlor residues continue to increase, they could contribute to deaths in future years. Authors believe that these insecticides are a major threat to the continued existence of this maternity colony.

Acknowledgments

We thank V. Brack, M. LaVal, and T. Zinn for field assistance and A. Federighi and L. Stickel for critical readings of the manuscript.

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Residues of Polychlorinated Biphenyls and DDT in Water and Sediment of the Indian River Lagoon, Florida—1977–78[1]

Tsen C. Wang, Robert S. Johnson,[2] and Joe L. Bricker

ABSTRACT

Water and sediment samples collected during 1977–78 from the Indian River lagoon between Vero Beach, Indian River County, and Fort Pierce, Saint Lucie County, Florida, were analyzed for PCBs and DDT. Sample locations were chosen on the basis of proximity to major tributaries, sewage outfalls, or municipal areas. Concentrations in water samples were below 0.01 ppb ΣDDT and 0.5 ppb PCBs. Small amounts of PCBs and DDT were found in most sediment samples, ranging from <1.0 ppb to 0.63 ppm Aroclor 1254 and from <0.1 ppb to 0.081 ppm ΣDDT. Samples from the Taylor Creek tributary and from the Fort Pierce power plant and municipal docking area contained higher PCB concentrations then did samples from other locations. DDT and PCB levels in most samples indicate little contamination by these compounds of the Indian River Waterway between Vero Beach and Fort Pierce.

Introduction

Polychlorinated biphenyls (PCBs) and ΣDDT are ubiquitous environmental contaminants. Reports of widespread distribution of organochlorine pesticide residues in the global ecosystem are increasing (*3–5, 8, 9, 11*). However, little information is available in the literature regarding organochlorine levels in the water and sediment of the Indian River lagoon.

The Indian River is a lagoonal estuary situated along the east central coast of Florida. This estuary extends 190 km, from Titusville, Brevard County, in the north to Saint Lucie Inlet, Martin County, in the south (Fig. 1). Authors investigated the occurrence of organochlorines in the Indian River lagoon between Vero Beach, Indian River County, and Fort Pierce, Saint Lucie County (Fig. 2), during 1977 and early 1978.

Methods and Materials

Figure 2 indicates approximate locations of seven sampling stations which were chosen on the basis of proximity to major tributaries, sewage plant outfalls, or municipal areas.

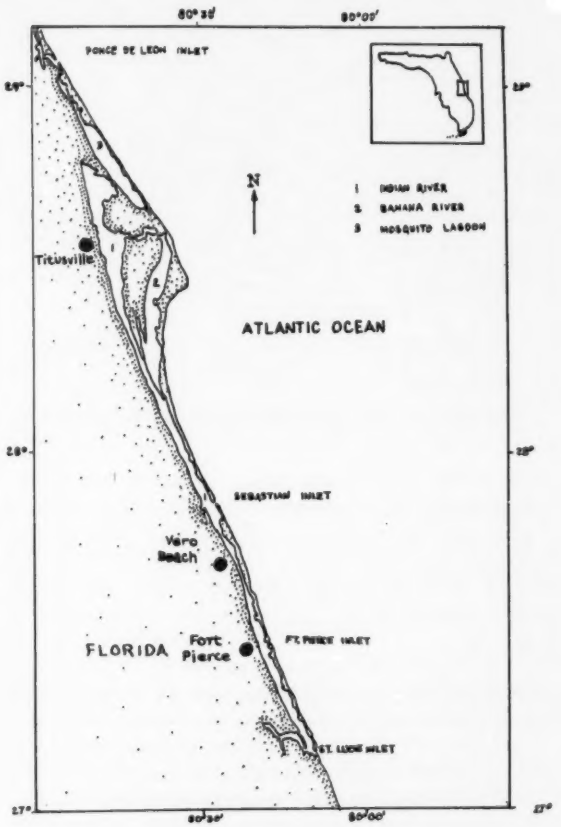

FIGURE 1. *Location of Indian River lagoon, Florida*

Surface water samples were collected at each station in a precleaned solvent bottle. The water samples were brought back to the authors' laboratory and refrigerated at 4°C overnight. Samples were analyzed the day after collection.

Each 3-liter water sample was drained at 250 ml/minute through a glass column containing 50 ml Amberlite XAD-2 resin (*2*). The column was eluted with 200 ml

[1] Harbor Branch Foundation, Inc., RR 1, Box 196, Fort Pierce, Fla. 33450. Contribution No. 163.
[2] Present address: Varian Corporation, Boston, Mass.

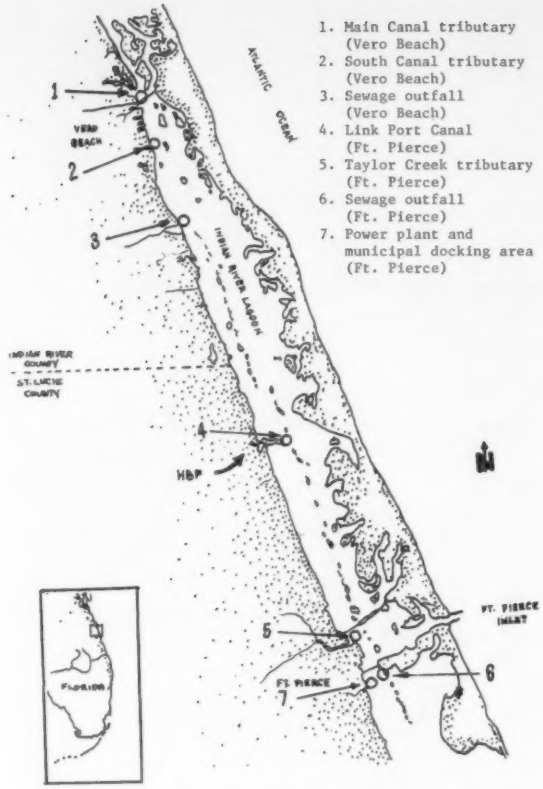

FIGURE 2. *Map of sampling stations, Indian River lagoon, Florida*

acetonitrile at full gravity flow, followed by 500 ml distilled water. The combined solvent was then extracted twice with 50 ml hexane. The hexane extracts were cleaned on a Florisil microcolumn (*6*) and eluted with 6.5 ml of 10 percent ethyl ether in hexane. The sample was concentrated to 1 ml before gas chromatographic analysis.

The 100-g composited sediment samples were air dried for about two days at ambient temperature. The sample was then shaken in a wrist-action shaker for 2 hours with isopropyl alcohol followed by hexane to recover the isopropyl alcohol together with the desorbed material. The extract was washed with distilled water, dried through a Na_2SO_4-Celite column and concentrated to 1 ml before cleanup (*10*). The hexane extract was passed through a Florisil column and eluted with 100 ml of 10 percent methylene chloride in hexane. PCBs were separated from chlorinated pesticides on a silicic acid column (*1*). Activated copper was added to remove any sulfur from the sediment extracts before they were applied to the silicic acid column. Residues in the samples were further treated with potassium hydroxide for confirmation and sample cleanup (*12*). The analytical scheme for sediment samples is shown in Figure 3.

Compounds were identified by gas-liquid chromatographic analysis and confirmed by thin-layer chromatography (*7*) when sample size and concentration were sufficient. Analyses were performed on a Perkin-Elmer Model 900 gas chromatograph with the following instrument parameters and operating conditions:

Detector:	^{63}Ni
Dual columns:	6 ft × 2 mm ID glass, packed with a mixture of 1.5 percent OV–17 and 1.95 percent QF–1; and a mixture of 4 percent SE–30 and 6 percent OV–210 on 100–120-mesh Chromosorb Q
Temperatures:	column 185°C injector 205°C detector 220°C
Carrier gas:	95 percent argon in methane flowing at 21 ml/minute.

The minimum detectable concentrations for Aroclor 1254 and DDT residues were 0.5 ppb and 0.01 ppb in water and 1.0 ppb and 0.10 ppb in sediment samples, respectively.

Recoveries

Water and sediment samples were spiked with 20 ng PCB and 75 pg ΣDDT. Duplicate analyses produced the following recoveries:

Compound	% Recovery	
	Water (± SD, $n = 5$)	Sediment (± SD, $n = 4$)
Aroclor 1254	95 ± 4	92 ± 4
o,p'-DDT	90 ± 10	91 ± 3
p,p'-DDT	92 ± 8	91 ± 8
p,p'-DDE	83 ± 15	98 ± 14
p,p'-TDE	90 ± 7	106 ± 21

The results reported in this paper were not corrected for these recoveries.

Results and Discussion

After water and sediment samples were collected from the Indian River lagoon, duplicate residue analyses were performed. The arithmetic means of PCB and ΣDDT concentrations for each sample are presented in Table 1. Residues ranging from <1.0 ppb to 0.63 ppm Aroclor 1254 and from <0.1 ppb to 0.081 ppm ΣDDT were detected in most sediment samples. However, PCB and ΣDDT residues were below detection limits in the water samples: less than 0.50 ppb Aroclor 1254 and 0.01 ppb ΣDDT.

Table 1 illustrates the amounts of PCB and ΣDDT found in the sediment samples. Main Canal and South Canal in Indian River County are two major tributaries to the lagoon through which agricultural runoff occurs. The results show that samples from the Main Canal tributary area had slightly higher PCB and ΣDDT content

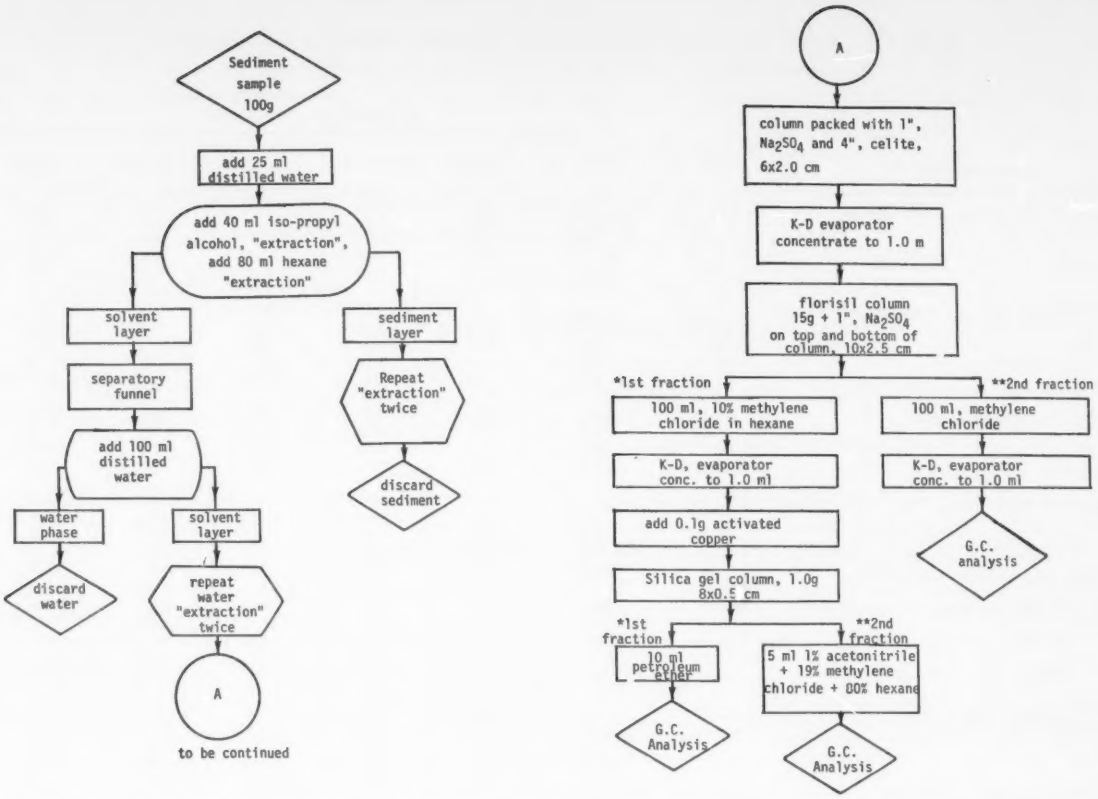
Sediment sample 100g
add 25 ml distilled water
add 40 ml iso-propyl alcohol, "extraction", add 80 ml hexane "extraction"
solvent layer
sediment layer
separatory funnel
Repeat "extraction" twice
add 100 ml distilled water
discard sediment
water phase
solvent layer
discard water
repeat water "extraction" twice
A
to be continued
A
column packed with 1", Na_2SO_4 and 4", celite, 6x2.0 cm
K-D evaporator concentrate to 1.0 m
florisil column 15g + 1", Na_2SO_4 on top and bottom of column, 10x2.5 cm
*1st fraction
**2nd fraction
100 ml, 10% methylene chloride in hexane
100 ml, methylene chloride
K-D, evaporator conc. to 1.0 ml
K-D, evaporator conc. to 1.0 ml
add 0.1g activated copper
G.C. analysis
Silica gel column, 1.0g 8x0.5 cm
*1st fraction
**2nd fraction
10 ml petroleum ether
5 ml 1% acetonitrile + 19% methylene chloride + 80% hexane
G.C. Analysis
G.C. Analysis

FIGURE 3. *Analytical scheme for cleanup and extraction of organochlorines from sediment samples from the Indian River lagoon, Florida*

than did samples from the South Canal tributary. PCB and ΣDDT residue concentrations in the Main Canal samples ranged from not detectable to 210 ppb and from not detectable to 5.62 ppb, respectively. Residue concentrations in South Canal samples ranged from not detectable to 8.67 ppb PCBs and from not detectable to 0.50 ppb ΣDDT. The frequency with which PCB and DDT appeared at both sampling sites was 60 percent. The Taylor Creek tributary in Saint Lucie County is another major source of agricultural runoff to the lagoon. Samples from Taylor Creek had the highest PCB residues in the study area. Residues ranged from 20 to 570 ppb Aroclor 1254 and from 0.96 to 19.9 ppb ΣDDT. Fort Pierce power plant and municipal docking area also had relatively high PCB and ΣDDT residues. Aroclor 1254 ranged from 39 to 278 ppb and ΣDDT from 1.90 to 81.0 ppb in the sediment samples. Both compounds were found in all samples from Taylor Creek and Fort Pierce municipal docking area. Samples from near the Vero Beach sewage outfall contained 1.0–16.2 ppb Aroclor 1254 with 100 percent frequency occurrence; ΣDDT levels ranged from not detectable to 0.38 ppb in 25 percent of samples. Residues in samples from near the Fort Pierce sewage outfall ranged from not detectable to 11.1 ppb Aroclor 1254 and from not detectable to 1.70 ppb ΣDDT. Of six samples analyzed, 83 percent contained both compounds.

Conclusions

Low concentrations of PCB and ΣDDT residues were found only in the sediment samples. Sediment samples collected from Taylor Creek tributary and Fort Pierce municipal docking area had higher PCB and ΣDDT residue levels than did other sample sites. The source of the compounds is not known. The data from this survey do not show any clear correlation between sampling site and sampling date.

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TABLE 1. *Polychlorinated biphenyls and ΣDDT residues in sediment of the Indian River lagoon between Vero Beach and Fort Pierce, Florida, 1977–78*

Sampling Site	Sampling Date	Residues, ppb Dry Weight					
		Aroclor 1254	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*p,p'*-DDT	ΣDDT
Main Canal tributary, Vero Beach	2–07–77	5.33	ND	ND	ND	ND	ND
	3–07–77	ND	ND	ND	ND	ND	ND
	4–18–77	ND	ND	0.96	2.40	ND	3.36
	1–11–78	210	ND	ND	2.13	ND	2.13
	4–12–78	20.76	4.51	ND	1.11	1.97	5.62
South Canal tributary, Vero Beach	2–07–77	8.67	ND	ND	ND	ND	ND
	3–07–77	1.95	ND	ND	ND	ND	ND
	4–18–77	ND	ND	ND	ND	ND	ND
	1–11–78	0.61	0.40	ND	0.10	ND	0.50
	4–12–78	ND	0.14	ND	0.09	0.10	0.33
Sewage outfall, Vero Beach	2–07–77	16.2	ND	ND	ND	ND	ND
	3–07–77	1.36	ND	ND	ND	ND	ND
	4–18–77	10.1	ND	ND	ND	ND	ND
	4–12–78	1.0	0.17	ND	0.21	ND	0.38
Link Port, Fort Pierce	2–07–77	23.7	ND	ND	ND	ND	ND
	3–07–77	2.5	ND	ND	ND	ND	ND
	12–15–77	ND	1.47	ND	1.80	ND	2.27
	1–11–78	1.89	0.07	ND	0.35	ND	0.42
	4–12–78	ND	0.03	ND	0.12	ND	0.15
Taylor Creek, Fort Pierce	2–07–77	20.6	ND	0.96	ND	ND	0.96
	3–07–77	32.3	ND	7.5	ND	ND	7.5
	4–18–77	82.0	1.1	3.5	3.5	0.2	8.3
	12–15–77	41.4	13.3	5.9	0.60	ND	19.9
	1–11–78	570	0.50	0.50	0.91	ND	10.01
Sewage outfall, Fort Pierce	2–07–77	1.44	ND	ND	ND	ND	ND
	3–07–77	11.1	ND	ND	0.5	ND	0.5
	4–18–77	5.0	ND	0.37	1.33	ND	1.70
	12–05–77	ND	0.15	ND	0.38	0.06	0.59
	1–11–78	3.1	0.28	ND	0.36	ND	0.64
	4–12–78	2.21	0.14	0.26	0.79	0.06	1.25
Fort Pierce power plant and municipal docking area	3–07–77	278	ND	1.9	ND	ND	1.90
	4–18–77	140	ND	6.2	16.5	ND	22.7
	12–15–77	39	13.3	5.99	33.1	28.6	81.0
	1–11–78	120	0.5	ND	1.00	3.20	4.70
	4–12–78	61	6.25	5.50	13.0	1.46	26.2

NOTE: ND = not detectable.

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Organochlorine Pesticide, PCB, and PBB Residues and Necropsy Data for Bald Eagles from 29 States—1975–77[1]

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ABSTRACT

During 1975–77, 168 bald eagles (Haliaeetus leucocephalus) *found moribund or dead in 29 states were analyzed for organochlorine pesticides and polychlorinated biphenyls (PCBs); 32 specimens from 13 states were analyzed for polybrominated biphenyls (PBBs). PCBs were present in 166 bald eagle carcasses and DDE was found in 165. TDE and dieldrin were identified in 137 samples,* trans-*nonachlor in 118, and oxychlordane in 90. Brains of five eagles contained possible lethal levels of dieldrin, and two eagles possibly died of endrin poisoning. Nine eagle livers, analyzed because of suspected lead poisoning, contained high levels of lead. Twenty percent of the eagles died from shooting, the most common cause of death; this cause of death, however, has declined.*

Introduction

This paper is the sixth in a series (*1, 2, 5–7*) evaluating pesticide residues and necropsy data on bald eagles (*Haliaeetus leucocephalus*), and it covers the years 1975–77.

Sampling and Necropsy

One hundred sixty-eight moribund or dead bald eagles were collected in 29 states (Table 1). Sampling, shipping, and storage procedures have been reported (*2*). Eagles found in the field were packed in Dry Ice and shipped air express to the Fish and Wildlife Service, U.S. Department of the Interior, National Wildlife Health Laboratory, Madison, Wisconsin, for necropsy (*1*). Following necropsy, the brain and the remaining carcass, except skin, feet, wings, liver, kidney, and gastrointestinal tract, were packed in Dry Ice and shipped air express to the Patuxent Wildlife Research Center, Laurel, Maryland, for chemical residue analysis.

Analytical Procedures

Sample preparation, extraction, lipid removal, and chemical separations have been reported (*2*). The procedure for eluting pesticides from the SilicAr column was modified to isolate dieldrin and endrin in a discrete fraction from the following number of samples: 8 of 49 eagles collected in 1975, 13 of 50 collected in 1976, and 52 of 69 collected in 1977. The modification involved collecting four fractions as follows:

Fraction 1: 80 ml petroleum ether, contained HCB and mirex

Fraction 2: 320 ml petroleum ether, contained PCBs, PBBs, and DDE

Fraction 3: 275 ml of 15 percent methylene chloride in hexane contained the remaining organochlorine compounds except endrin and dieldrin

Fraction 4: 200 ml mixture of 1 percent acetonitrile, 19 percent hexane, and 80 percent methylene chloride, contained endrin and dieldrin.

TABLE 1. *Distribution, by state and year of death, of bald eagles collected during 1975–77*

State	No. of Eagles Collected		
	1975	1976	1977
Alaska	3	5	5
California	2		
Colorado		1	4
Florida	7	2	4
Georgia			1
Idaho			2
Illinois			1
Indiana		1	
Iowa	5	2	1
Kansas		3	3
Maine	3	1	4
Maryland	2	2	
Michigan	4	1	1
Minnesota	2	4	7
Missouri		5	2
Nebraska	5	9	5
New Mexico	2		
New York		1	
Ohio	1	1	
Oklahoma	2	2	1
Pennsylvania			1
South Carolina			1
South Dakota	1	2	4
Texas	1		
Utah	2	2	11
Virginia	3		1
Washington		1	
Wisconsin	4	5	9
Wyoming			1
TOTAL	49	50	69

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Other compounds normally analyzed for were chlordane, DDT, heptachlor epoxide, nonachlor, oxychlordane, TDE, and toxaphene. Samples were analyzed on a Hewlett-Packard Model 5713 or 5840A gas-liquid chromatograph equipped with a Ni^{63} detector, automatic sampler, and digital processor. The first 21 samples received in 1975 were analyzed on column 1. The remainder of the 1975 samples and all 1976 and 1977 samples were analyzed on column 2 to effect a separation of *cis*-chlordane and *trans*-nonachlor. Instrument parameters and operating conditions were:

Columns:	(1) 1.83 m × 4 mm ID, packed with a mixture of 4 percent SE–30 and 6 percent QF–1 (2) 1.83 m × 4 mm ID, packed with a mixture of 1.5 percent OV–17 and 1.95 percent QF–1
Temperature:	columns 190°C
Carrier gas:	5 percent methane in argon, flowing at 60 ml/minute

Fraction 2, which was analyzed for PBBs, was gas chromatographed on a 3 percent OV–1 column at 245°C with a 100-ml/minute flow rate. Under these conditions, the hexabromobiphenyl (HBBP) compound eluted after the PCBs. The pesticides were measured by digital integration of peak areas; PCBs were estimated by comparing total peak area with that of Aroclor 1254 or 1260, depending on the gas chromatographic profile of the sample. PBB values were based on the HBBP peak. Toxaphene measurements were semiquantitative estimates made from two peak areas as previously described (*6*).

Average percentage recoveries from spiked pheasant carcass tissue were: DDE, 104; TDE, 92; DDT, 100; dieldrin, 89; heptachlor epoxide, 93; oxychlordane, 92; *cis*-chlordane, 92; *trans*-nonachlor, 91; endrin, 90; HCB, 80; mirex, 90; and Aroclor 1260, 90. Residue levels were not corrected for recovery. The lower limit of reportable residues was 0.05 ppm pesticides, 0.10 ppm PCBs, and 0.02 ppm PBBs.

Residues in 56 specimens, or 33 percent, were confirmed on an LKB 9000 or a Finnigan 4000 series gas chromatograph/mass spectrometer (GC/MS). Operating parameters for the LKB have been described (*1*). The procedures followed with the Finnigan model were:

Column:	1.83 m × 2 mm ID, packed with a mixture of 1.9 percent OV–17 and 1.95 percent QF–1	
Temperatures:	column	programmed at 2°C/minute from 140°C to 225°C
	injector	215°C
	separator	235°C
	ion source	300°C
Carrier gas:	helium flowing at 30 ml/minute	

Results and Discussion

Table 2 shows the results of the tissue analyses of the 168 bald eagles. PCBs were present in 166 carcass samples, DDE in 165, and dieldrin in 137. Thirty-two of the 69 specimens collected during 1977 were examined for PBBs; low residue levels were detected in 11 specimens from Maine, Virginia, Florida, Missouri, Minnesota, and Wisconsin.

A comparison of residue data from year to year is difficult because a systematic sampling procedure could not be considered and also because of the wide range of residue levels. However, median values for DDE, dieldrin, and PCBs in the carcasses collected during 1977 were lower than in any previous year (*1, 2, 5–7*). During 1972–77, the frequency of detection of residues in the brains of this species has steadily declined as follows: DDE from 100 to 83 percent, dieldrin from 67 to 46 percent, and PCBs from 92 to 84 percent.

Five eagles may have died of dieldrin poisoning (Table 3). Dieldrin levels in the brains ranged from 6.8 to 11.0 ppm. A study of several series of experimental birds killed by dieldrin indicated that when death was primarily caused by the neurotoxic action of dieldrin, the lower end of the distribution curve fell at about 5 ppm (unpublished data: W. H. Stickel (Patuxent Widlife Research Center, Laurel, Md.), November 27, 1978). The study concluded that death may be due to dieldrin poisoning at the 5 ppm level but that the probability of dieldrin-caused mortality increases as the levels increase; at 9 ppm and above, the probability of dieldrin poisoning is high.

The 11-ppm reading of the present study was from an immature female collected in Wisconsin. The bird was weak, unable to fly, and died the next day. It had no subcutaneous or abdominal fat; the coronary fat was undergoing resorption and the pectoral muscles were reduced. Bacteriological and virological tests were negative.

In two possible cases of death caused by endrin poisoning (Table 3), brains contained 0.71 ppm and 1.2 ppm endrin. The known lethal range begins at about 0.6 ppm, and evidence of death caused by endrin becomes strong at 0.8 ppm, as reported by Stickel et al. (*8*). Neither of the two eagles had subcutaneous, abdominal, or coronary fat. The lack of fat is often seen in organochlorine pesticide poisoning, although it can be caused by other factors.

Livers of specimens that had lead shot pellets in the stomach, were emaciated, or had signs of diarrhea were analyzed for lead by the Central Animal Health Laboratory, Madison, Wisconsin. High levels were found in nine specimens (Table 4), suggesting lead poisoning. However, the lethal level of lead in bald eagles is not known and is currently being studied. Longcore (*4*) concluded

TABLE 2. *Residues of organochlorine pesticides, PCBs, and PBBs in 168 bald eagles from 29 states, 1975–77*

Compound	Year	Residues, ppm Wet Weight					
		Carcass			Brain		
		No. of Specimens [1]	Median	Range	No. of Specimens [1]	Median	Range
p,p'-DDE	1975	49	4.5	0.17– 74.0	45	0.81	0.05– 35.0
	1976	49	6.8	0.18–120.0	42	0.93	0.07– 52.0
	1977	67	4.0	0.10– 65.0	57	0.98	0.05–100.0
p,p'-TDE	1975	44	0.42	0.05– 10.0	18	0.51	0.07– 1.9
	1976	43	0.45	0.08– 12.0	14	0.32	0.06– 1.2
	1977	50	0.26	0.06– 4.5	19	0.23	0.05– 2.3
p,p'-DDT	1975	13	0.11	0.06– 0.73	4	0.07	0.05– 0.09
	1976	12	0.13	0.05– 0.58	1	0.05	
	1977	6	0.09	0.06– 0.12	2	0.10	0.06– 0.13
Dieldrin	1975	44	0.60	0.06– 12.0	32	0.23	0.05– 11.0
	1976	40	0.66	0.05– 12.0	25	0.38	0.05– 9.8
	1977	53	0.22	0.05– 4.0	32	0.27	0.05– 6.8
Heptachlor epoxide	1975	27	0.17	0.05– 1.8	11	0.22	0.07– 1.6
	1976	29	0.15	0.05– 2.8	12	0.17	0.05– 2.1
	1977	29	0.11	0.05– 1.4	14	0.18	0.05– 0.77
Oxychlordane	1975	28	0.18	0.05– 0.78	15	0.23	0.07– 0.68
	1976	28	0.14	0.06– 2.3	12	0.18	0.06– 2.6
	1977	34	0.13	0.05– 1.2	16	0.29	0.08– 1.7
cis-Chlordane and/or *trans*-nonachlor	1975	17[2]	0.55	0.11– 6.5	13	0.11	0.05– 3.1
cis-Chlordane	1975	20[3]	0.32	0.11– 4.5	9	0.19	0.07– 1.3
	1976	27	0.24	0.05– 1.7	13	0.09	0.05– 1.2
	1977	19	0.22	0.07– 2.2	20	0.19	0.06– 6.4
trans-Nonachlor	1975	26[3]	0.38	0.06– 6.0	13	0.20	0.06– 2.2
	1976	41	0.38	0.05– 4.0	18	0.22	0.06– 3.4
	1977	51	0.28	0.05– 5.6	22	0.33	0.05– 7.4
cis-Nonachlor	1975	29	0.14	0.05– 1.7	12	0.17	0.06– 0.75
	1976	27	0.10	0.05– 0.83	9	0.13	0.05– 0.41
	1977	30	0.15	0.05– 1.3	14	0.17	0.06– 4.0
Endrin	1975	5[4]	0.16	0.09– 1.0	3	0.44	0.12– 0.50
	1976	6	0.48	0.18– 3.0	6	0.32	0.15– 0.71
	1977	5	0.07	0.06– 2.5	5	0.14	0.05– 1.2
Toxaphene	1975	20	0.30	0.06– 2.5	8	0.24	0.13– 1.2
	1976	11	0.11	0.05– 0.55	7	0.25	0.05– 0.31
	1977	22	0.22	0.06– 0.88	13	0.16	0.06– 2.7
HCB	1975	11	0.08	0.05– 0.12	4	0.06	0.05– 0.07
	1976	8	0.08	0.05– 0.40	4	0.07	0.05– 0.16
	1977	4	0.08	0.07– 0.12	6	0.06	0.05– 0.17
Mirex	1975	22	0.19	0.06– 1.9	13	0.14	0.06– 0.98
	1976	24	0.24	0.05– 2.5	8	0.13	0.09– 0.57
	1977	29	0.25	0.05– 5.3	18	0.21	0.05– 5.5
PBBs	1977	10[5]	0.07	0.03– 0.27	7	0.05	0.03– 0.17
PCBs	1975	49	7.7	0.20–220.0	46	1.2	0.13–160.0
	1976	50	12.0	0.18–560.0	44	2.2	0.10–240.0
	1977	67	5.5	0.21–190.0	58	1.5	0.07–160.0

[1] Number of specimens containing residues; median is based on this number. Total samples numbered 49 in 1975, 50 in 1976, and 69 in 1977.
[2] Twenty of the 49 specimens were analyzed for *cis*-chlordane and/or *trans*-nonachlor.
[3] Twenty-nine of the 49 specimens were analyzed separately for *cis*-chlordane and for *trans*-nonachlor.
[4] Twenty-nine of the 49 specimens were analyzed for endrin.
[5] Thirty-two of the 69 specimens were analyzed for PBBs.

from experimental studies, and from results reported in the literature for lead-poisoned waterfowl, that 6–20 ppm lead in the liver of mallards indicated acute exposure to lead. The two eagles from northern California were observed regurgitating a fluorescent green material and were found dead the next day. Necropsy failed to indicate cause of death but both esophagi were stained with bile. Livers contained 38 ppm and 29 ppm lead. Organochlorine residues in carcasses and brains were low. The Maryland specimen that contained 75 lead shot pellets in the stomach has been studied in detail by Jacobsen et al. (*3*).

TABLE 3. *Data on five suspected cases of dieldrin poisoning and two suspected cases of endrin poisoning of bald eagles from six states, 1975–77*

State	Year	Sex	Age	Residues in Brain, ppm	Necropsy Findings [1]
			DIELDRIN		
Minnesota	1975	M	adult	7.5	Open; no fat deposits
Wisconsin	1975	F	immature	11.0	Open; no fat deposits
Missouri	1976	F	immature	9.8	Emaciation; no fat deposits
Florida	1976	M	immature	8.7	Open; no fat deposits
Wisconsin	1977	F	adult	6.8	Open; no fat deposits
			ENDRIN		
Minnesota	1976	M	adult	0.71	Open; no fat deposits
Iowa	1977	M	immature	1.2	Open; no fat deposits

[1] Open = No diagnosis could be made on the basis of necropsy findings.

TABLE 4. *Data on nine bald eagles that contained high lead levels in the liver, 1975–77*

State	Year	Sex	Age	Residue in Liver, ppm	Necropsy Findings
California	1975	F	adult	38.1[1]	Open; bile-stained esophagus
California	1976	F	adult	29.0[1]	Open; bile-stained esophagus
Florida	1975	F	adult	26.2	Open
Maine	1975	F	adult	34.0	Open; nine shot pellets in bile-stained stomach
Nebraska	1976	F	adult	23.7	Open; one pellet in stomach
Maryland	1976	F	immature	22.9	Open; 75 shot pellets in stomach
South Dakota	1976	F	adult	36.9	Open; no fat, intestine filled with bile
South Dakota	1977	M	adult	28.0	Open; no fat
Wisconsin	1977	M	immature	30.4	Open; no fat, liver stained green with bile

[1] Analysis at Patuxent Wildlife Research Center, Laurel, Maryland; remainder analyzed by Central Animal Health Laboratory, Wisconsin Department of Agriculture, Madison, Wisconsin for National Wildlife Health Laboratory.

TABLE 5. *Probable causes of death of 168 bald eagles collected in 29 states, 1975–77*

Cause of Death	No. of Eagles
Shot	33
Impact injuries	22
Electrocution	17
Lead poisoning	9
Pneumonia	6
Trapping wounds	6
Dieldrin poisoning	5
Drowning	3
Peritonitis	3
Endrin poisoning	2
Enteritis	2
Septicemia	2
Strychnine poisoning	2
Aspiration of fish	1
Avian cholera	1
Aspergillosis	1
Cyanide poisoning [1]	1
Dieldrin/pneumonia	1
Hepatic necrosis	1
Impaction of cloaca and large intestine	1
Laceration of lung	1
Myocardial infarction	1
Penetration wound	1
Open [2]	46
TOTAL	168

[1] Cyanide analysis was performed by Central Animal Health Laboratory, Wisconsin Department of Agriculture, Madison, Wisconsin.
[2] No diagnosis could be made on the basis of necropsy findings or chemical analysis.

Shooting remained the most frequent cause of death, but the proportion of mortalities due to shooting has declined steadily: 1966–68, 41 percent; 1969–70, 46 percent; 1971–72, 35 percent; 1973–74, 24 percent; and 1975–77, 2 percent (Table 5).

Conclusions

The presence of organochlorine residues, some at known lethal levels, in bald eagles shows the continuing influence of contamination on the environment. The data indicate that the residue levels are declining.

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SOILS

Heavy Metal Concentrations in Soils of Five United States Cities, 1972 Urban Soils Monitoring Program

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ABSTRACT

Lead, mercury, cadmium, and arsenic levels were determined in soil samples from Des Moines, Iowa, Fitchburg, Massachusetts, Lake Charles, Louisiana, and Reading and Pittsburgh, Pennsylvania, as part of the 1972 Urban Soils Monitoring Program. Sampling sites within each Standard Metropolitan Statistical Area (SMSA) were defined as urban or suburban based on their position either within or outside the official city limits, respectively. In addition, each site was classified lawn or waste according to the maintenance it received. Except in Fitchburg, urban soils of each SMSA contained significantly higher mean concentrations of cadmium, lead, and mercury than did suburban soils. Mean urban soil concentrations of arsenic were similar to suburban concentrations in each SMSA except Des Moines and Reading, where urban levels were significantly higher. Generally, the metal concentrations in lawn and waste areas did not differ significantly. The results indicate a general contamination of these areas, probably as a result of fallout of airborne metal aerosols from industrial processes and/or fossil-fuel combustion.

Introduction

Although arsenic, cadmium, lead, and mercury occur naturally, they can be detrimental to plant and animal life at high concentrations. Industrial wastes, auto emissions, and pesticide and fertilizer applications (*5, 6*) all contribute to heavy metal contamination of soils. Trace element contamination of urban soils is often from many sources (*18*).

Lead concentrations from these sources are generally highest in the surface soil layers and decrease rapidly with either soil depth or distance from the surface (*1, 7, 12, 16*). The lead content of soils near highways increases with increased traffic volume (*1, 7, 15, 24*).

Mercury accumulates in soil via various industrial processes, pesticide use, and the combustion of fossil fuels (*20, 24*).

Cadmium contamination of the soil occurs through the use of phosphate fertilizers and cadmium-containing pesticides, and through the discharge of liquid or solid waste from metallurgical and industrial activities (*12, 17*). Higher traffic volumes in urban areas probably contribute to the cadmium burden in urban soils because cadmium is used in lubricating oils, diesel fuel, and tires (*13*). Urban refuse disposal is another likely source because cadmium is a component of both paper and plastics, which comprise a major portion of urban solid waste (*17*).

The main sources of arsenic contamination are metal smelting and combustion of fossil fuels (*14*), and pesticide applications (*9, 10*).

The present study was undertaken as part of the U.S. Environmental Protection Agency's Urban Soils Monitoring Program. Reported here are arsenic, cadmium, lead, and mercury concentrations detected during 1972 in soils of five United States Standard Metropolitan Statistical Areas (SMSAs), including Des Moines, Iowa; Fitchburg, Massachusetts; Lake Charles, Louisiana; and Reading and Pittsburgh, Pennsylvania.

Sampling Procedures

Five SMSAs were randomly selected from a list provided by the Bureau of the Census, U.S. Department of Commerce (*23*). Within each SMSA, sampling sites were randomly allocated within the city limits to yield

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a density of one site per 2.6 km^2 or one square mile and were designated as urban sites. In the remainder of the SMSAs, sites were randomly allocated to yield a density of one site per 51.8 km^2 or 20 square miles and were designated as suburban sites. In addition, each site was described as either lawn or waste according to the criteria used by Wiersma et al. (*26*) to indicate whether the site received regular maintenance.

All sampling sites were 231 m^2, usually a 15.2 m by 15.2 m plot (50 ft by 50 ft). Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm deep, were collected throughout the site on a 4 by 4 grid pattern. The cores were composited, sieved three times through a 6.3-mm galvanized mesh screen, and thoroughly mixed. A 2.3-liter subsample was drawn, packed in a new metal paint can which had been rinsed previously with isopropyl alcohol, and was shipped to the Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi. When the samples arrived at the laboratory, soil for analysis was removed from the center of the cans to minimize any possible contamination from the cans.

Analytical Procedures

All metals were determined by atomic absorption spectrophotometry. For arsenic analysis, the soil sample was extracted with 9.6*N* HCl, and arsenic was reduced to As^{+3}. As^{+3} was partitioned from the acid to benzene, and then further partitioned from benzene to water for the absorption measurement. A Perkin-Elmer Model 303 spectrophotometer was used, and absorbance was measured with an arsenic cathode lamp at 197.0 nm with argon as an aspirant to an air-hydrogen flame. Average recovery was 56 percent arsenic. Concentrations were corrected for recovery; minimum detection limit, after correction, was 0.2 ppm.

For cadmium, lead, and mercury analyses, soil samples were dried at 50°C for 24 hours. A 10-g dry soil sample was weighed into a 125-ml Erlenmeyer flask, and 100 ml of a mixture of 4*N* HNO_3 and 0.7*N* HCl was added. The capped flask was swirled and heated at 70–90°C for 2 hours in a water bath. After the mixture cooled and settled, cadmium and lead were determined on a Perkin-Elmer Model 306 spectrophotometer with direct aspiration and an air-acetylene flame. Absorbance was measured at 229.0 nm for lead and at 283.3 nm for cadmium with background corrections. Lead recovery averaged 90–95 percent with a detection limit of 0.5 μg/ml, equivalent to 0.5 ppm in 1 g of soil. Cadmium recovery averaged 85–90 percent with a detection limit of 0.5 μg/ml, equivalent to 0.5 ppm in 1 g of soil.

For the mercury determination, an aliquot of the acid extract, containing not more than 0.5 μg mercury, was pipetted into a 300-ml BOD bottle. Five milliliters of concentrated H_2SO_4 were added to the aliquot, and the volume was adjusted to 100 ml. Flameless AA by the method of Hatch and Ott (*8*) was followed. Mercury recovery averaged 60–100 percent, depending on soil type and percent organic matter. The detection limit was 0.05 μg/100 ml, equivalent to 0.2 ppm in 1 g of soil.

Values for all four metals were corrected for the appropriate percent recovery, as determined by recovery studies carried out in conjunction with the analyses. The recovery studies included fortifying selected samples with known quantities of each metal followed by analysis and determination of the amount recovered.

Results

Results of the metal analyses are presented in Tables 1 and 2. Both tables list the number of analyses for each category, percent occurrence of the element, the arithmetic mean, the estimated geometric mean, and the minimum and maximum positive concentrations detected within each metropolitan area.

The estimated geometric mean is routinely presented in the tables as an alternative to the arithmetic mean as a measure of central tendency of the data. Such data are seldom distributed normally, as shown by tests for skewness and/or kurtosis, but often approximate a log-normal distribution. The log $(X + 0.01)$ transformation was used to determine the logarithmic means. The antilogs of these figures, minus 0.01, were taken to estimate the geometric mean in the untransformed dimension. Differences between means were checked for significance by t-tests of the transformed variate log $(X + 0.01)$.

LEAD

All soil samples contained detectable amounts of lead. Geometric means for the SMSAs ranged from 12 ppm at Lake Charles to 71 ppm at Pittsburgh. Individual sample measurements ranged from 2.1 ppm in a Lake Charles sample to 11,700 ppm in a Reading sample. Most published estimates show that lead occurs naturally in soils at levels of 10–20 ppm (*13, 22*). Urban portions of each SMSA, except Fitchburg, had significantly higher mean concentrations of lead than did corresponding suburban portions. Lead concentrations were similar in urban lawn and waste areas of all cities except Des Moines, where lead concentrations were significantly higher in lawn areas than in waste areas. Suburban lawn and waste lead concentrations were similar except in Reading, which had significantly higher lead levels in waste areas than in lawn areas.

MERCURY

Mercury was detected in 68 percent of the samples, ranging from 0.02 to 15 ppm. The highest geometric mean concentration for the SMSAs was 0.25 ppm in Fitchburg; the lowest was 0.01 ppm at Lake Charles. Average mercury concentrations in soils in the United

TABLE 1. *Heavy metal concentrations in urban and suburban soils of five Standard Metropolitan Statistical Areas, 1972—Urban Soils Monitoring Program*

Location	No. of Samples		Heavy Metal	Concentration, ppm Dry Weight			Samples Containing Detectable Amounts
	Urban	Suburban		Arithmetic Mean	Estimated Geometric Mean	Extreme Positive Values	
Des Moines, Iowa	59	25	Lead				
			urban	89.0	55.0	9.8 – 488.0	100
			suburban	15.0	14.0**	7.2 – 26.0	100
			Mercury				
			urban	0.44	0.10	0.06– 15.0	80
			suburban	0.01	<0.01**	0.06– 0.15	16
			Cadmium				
			urban	0.89	0.64	0.1 – 3.6	100
			suburban	0.28	0.12**	0.1 – 1.8	80
			Arsenic				
			urban	12.0	7.1	1.36– 119.0	98
			suburban	2.8	2.2**	0.40– 14.0	100
Fitchburg, Mass.	26	10	Lead				
			urban	117.0	62.0	12.0 – 1230.0	100
			suburban	60.0	34.0	4.4 – 278.0	100
			Mercury				
			urban	0.34	0.29	0.08– 0.83	100
			suburban	0.24	0.17	0.70– 0.50	90
			Cadmium				
			urban	0.13	0.06	0.12– 0.70	62
			suburban	0.13	0.05	0.11– 0.38	60
			Arsenic				
			urban	15.0	9.1	2.8 – 158.0	100
			suburban	7.4	5.8	2.0 – 18.0	100
Lake Charles, La.	16	54	Lead				
			urban	139.0	39.0	3.5 – 1330.0	100
			suburban	11.0	8.7**	2.1 – 61.0	100
			Mercury				
			urban	0.06	0.02	0.04– 0.29	50
			suburban	0.01	<0.01**	0.04– 0.18	7
			Cadmium				
			urban	0.36	0.02	0.11– 5.3	25
			suburban	0.01	<0.01*	0.11– 0.1	7
			Arsenic				
			urban	1.8	1.6	0.88– 5.7	100
			suburban	2.2	1.9	0.69– 8.2	100
Pittsburgh, Pa.	51	138	Lead				
			urban	444.0	267.0	45.0 – 2290.0	100
			suburban	52.0	44.0**	15.0 – 402.0	100
			Mercury				
			urban	0.64	0.46	0.1 – 2.1	100
			suburban	0.09	0.04**	0.02– 0.74	68
			Cadmium				
			urban	1.2	0.74	0.11– 4.9	98
			suburban	0.9	0.45*	0.11– 8.0	93
			Arsenic				
			urban	15.0	12.0	3.2 – 54.0	100
			suburban	15.0	13.0	3.6 – 122.0	100
Reading, Pa.	10	41	Lead				
			urban	1400.0	172.0	21.0 –11,700.0	100
			suburban	40.0	40.0**	14.0 – 306.0	100
			Mercury				
			urban	0.63	0.29	0.04– 2.8	100
			suburban	0.10	0.07**	0.04– 0.4	93
			Cadmium				
			urban	0.63	0.26	0.11– 1.7	90
			suburban	0.25	0.04*	0.11– 2.5	44
			Arsenic				
			urban	16.0	13.0	4.3 – 42.0	100
			suburban	8.6	7.0**	1.6 – 33.0	100

NOTE: Statistical significance of urban-suburban differences based on t-tests of the transformed variate log (X + 0.01), U.S. Environmental Protection Agency.
* Differences statistically significant (P = 0.05).
** Differences statistically significant (P = 0.01).

TABLE 2. *Heavy metal concentrations in lawn and waste soils of five Standard Metropolitan Statistical Areas, 1972—Urban Soils Monitoring Program*

Location	Area	No. of Sites	Concentration, ppm Dry Weight							
			Lead		Mercury		Cadmium		Arsenic	
			Arithmetic Mean	Geometric Mean	Arithmetic Mean	Geometric Mean	Arithmetic Mean	Geometric Mean	Arithmetic Mean	Geometric Mean
Des Moines, Iowa	Urban									
	lawn	39	102.0	68.0	0.61	0.14	0.85	0.68	14.7	9.9
	waste	20	65.0	38.0	0.11	0.05*	0.96	0.57	5.5	3.7**
	Suburban									
	lawn	15	13.0	12.0	ND	—	0.14	0.08	2.2	2.1
	waste	10	18.0	16.0	0.04	0.01	0.48	0.23	3.5	2.1
Fitchburg, Mass.	Urban									
	lawn	7	119.0	80.0	0.44	0.37	0.18	0.05	13.0	12.4
	waste	19	116.0	56.0	0.30	0.26	0.10	0.05	15.4	8.2
	Suburban									
	lawn	1	56.0	—	0.31	—	0.12	—	5.4	—
	waste	9	60.0	32.0	0.23	0.16	0.14	0.05	7.7	5.9
Lake Charles, La.	Urban									
	lawn	9	224.0	68.0	0.09	0.03	0.63	0.03	2.3	1.9
	waste	7	29.0	19.0	0.02	0.01	0.02	<0.01	1.2	1.2
	Suburban									
	lawn	20	9.7	7.3	0.01	<0.01	0.01	<0.01	1.7	1.6
	waste	34	11.0	9.7	0.01	<0.01	0.01	<0.01	2.5	2.1
Pittsburgh, Pa.	Urban									
	lawn	22	398.0	219.0	0.51	0.38	1.2	0.79	11.9	10.1
	waste	29	480.0	310.0	0.74	0.53	1.2	0.71	17.0	13.4
	Suburban									
	lawn	14	75.0	51.0	0.08	0.02	0.93	0.64	21.0	15.1
	waste	123	49.0	43.0	0.09	0.05	0.90	0.43	13.9	12.9
Reading, Pa.	Urban									
	lawn	1	48.0	—	0.11	—	0.11	—	16.4	—
	waste	9	1550.0	198.0	0.69	0.32	0.68	0.29	15.7	12.7
	Suburban									
	lawn	15	28.0	26.0	0.06	0.05	0.03	0.01**	8.4	7.5
	waste	26	72.0	50.0**	0.12	0.09	0.38	0.09**	8.7	6.8

NOTE: ND = Not detected.
Statistical significance based on t-tests of the transformed variate log (X + 0.01), U.S. Environmental Protection Agency.
* Differences statistically significant (P = 0.05).
** Differences statistically significant (P = 0.01).

States are reported to be about 0.07 ppm (*19, 25*). Urban portions of each SMSA, except Fitchburg, had significantly higher mean mercury concentrations than did corresponding suburban portions. Mercury concentrations were not significantly different between lawn and waste areas of either urban or suburban parts of any SMSA except in Des Moines, where the mean mercury concentration in lawn sites was significantly higher than in waste sites.

CADMIUM

Cadmium was detected in 73 percent of the samples, ranging from 0.11 to 8.0 ppm. Geometric mean concentrations for the SMSAs ranged from less than 0.01 ppm at Lake Charles to 0.52 ppm at Pittsburgh. Cadmium occurs naturally in soils at average concentrations of about 0.06 ppm (*14*). As with mercury and lead, mean cadmium concentrations were significantly higher at urban sites except in Fitchburg. The only significant differences in cadmium concentrations between lawn and waste sites were found in suburban Reading, where concentrations were significantly higher in lawn areas than in waste areas.

ARSENIC

Arsenic was detected in 99.8 percent of the samples, at levels of 0.58–158 ppm. Geometric mean concentrations for the SMSAs ranged from 1.9 ppm at Lake Charles to 13 ppm in Pittsburgh. Arsenic occurs naturally in soil at an average concentration of 6 ppm (*3, 14, 26*). Urban and suburban arsenic concentrations were not significantly different for the SMSAs except in Des Moines and Reading, where urban concentrations were significantly higher than suburban concentrations. Urban lawn sites in Des Moines also contained significantly higher arsenic concentrations than did urban waste areas. In all other comparisons of lawn and waste areas of suburban and urban portions, no significant differences were detected.

Discussion

Other investigators have attributed elevated metal concentrations in urban soils to atmospheric fallout of aerosols from industrial processes and fossil-fuel combustion, especially motor vehicle emissions (*2, 4, 5, 11, 21*). The present study supports previous findings. Such sources

would normally occur less frequently in suburban areas and would, therefore, result in lower suburban soil metal concentrations, as shown in the present study.

Urban and suburban mean soil concentrations of metals in Fitchburg may be similar because the city limits there do not seem to separate areas of more and less dense population and industry. The city of Leominster and several towns are included in that portion of the SMSA designated as suburban.

Mercury concentrations in Fitchburg were high compared to mercury concentrations in the other four cities. Mercury compounds were registered for fungicidal uses before 1972, and many industries in Fitchburg are types which would have used mercurial fungicides before 1972. These concentrations also might have originated from higher background soil concentrations of mercury, as suggested by the results of Shacklette et al. (*19*).

Summary and Conclusions

This study shows that metal concentrations in urban soils of SMSAs are generally higher than concentrations in the corresponding suburban soils. The similarity of average metal concentrations in lawn and waste sites within urban and suburban areas of these SMSAs indicates a general contamination of these areas. The main source of this contamination appears to be fallout of airborne metal aerosols from industrial processes and/or fossil-fuel combustion.

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WATER

Pesticides and PCB Residues in the Black Creek Watershed, Allen County, Indiana—1977–78 [1]

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ABSTRACT

The aquatic environment of a small agricultural drainage in northeastern Indiana was surveyed during 1977–78 for pesticide and PCB contamination. A total of 45 water, sediment, and fish samples from Black Creek watershed, Allen County, Indiana were analyzed for seven pesticides and PCBs. Low levels of dieldrin (mean 0.023 μg/g) and DDE (mean 0.016 μg/g) were found in all fish samples, but were not detected in water or sediment samples. PCB concentrations in fish were five times greater (0.102 μg/g) than were organochlorine pesticide concentrations. Two of seven water samples contained PCBs at 0.4 μg/liter and 0.2 μg/liter. Only the herbicide 2,4,5-T occurred in surface water samples during low stream discharge, at concentrations of 0.2–7.7 μg/liter. Atrazine, alachlor, carbofuran, and malathion were not detected in any samples.

Introduction

The 48.5 km² Black Creek watershed in Allen County, Indiana, is typical of the land use, topography, and soils of the larger Maumee River basin. Land use is 80 percent row crop agriculture and 4 percent urban.

A survey of the pesticide and PCB content of the water, sediment, and fish of this small agricultural drainage was conducted in 1977. The study was a portion of a research and demonstration project designed to identify and reduce agricultural sources of non-point pollution (*3*). The purpose of the survey was to assess toxic substance contamination of the aquatic environment at low stream discharge, and the results are presented here.

Sampling Procedures

On July 18 and 19, 1977, 14 sediment samples, 7 water samples, and 18 fish samples were collected from various locations in the Black Creek drainage. The 39 samples were analyzed for PCBs (Aroclors 1242 and 1254), dieldrin, DDE, atrazine, alachlor, carbofuran, malathion, and 2,4,5-T. Grab water and sediment samples were collected in one-quart wide-mouth glass jars that had been rinsed with acetone. Sediment samples were collected by directly scooping the top 10 cm of bottom material into the glass jars. A single fish species, creek chub (*Semotilus atromaculatus*), was collected by seining, and individuals were analyzed separately. Sediment and water samples were placed on ice and refrigerated until analysis. Fish specimens were frozen at −20°C and analyzed as received after thawing. Samples were held no longer than 50 days before analysis. On June 5, 1978, six water samples were collected and analyzed for 2,4,5-T only.

Analytical Procedures

All laboratory work was done at the Pesticide Laboratory of the Section of Wildlife Research, Illinois Natural History Survey. Analytical and cleanup procedures outlined in the *Pesticide Analytical Manual* of the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*5*) were followed for each compound.

Compounds were extracted from the water samples by extracting each 1-liter sample with three 100-ml aliquots of methylene chloride. The combined extracts were dried with sodium sulfate and concentrated to 1 ml by refluxing under a three-ball Snyder column. The compounds were then partitioned into an equivalent volume of ethyl acetate for injection into the gas chromatograph.

The compounds were extracted from sediment samples by mixing 50 grams of sediment with 100 ml ethyl acetate on a magnetic stirrer for 1 hour. The ethyl acetate was decanted with rinsing, reduced in volume, dried

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over anhydrous sodium sulfate, and dissolved in hexane for injection into the gas chromatograph.

Twenty-gram subsamples representative of the whole fish were pulverized in a blender with 100 ml acetonitrile. The acetonitrile was swirled with 10 ml hexane to remove fish oil, blown dry with nitrogen, and dissolved in ethyl acetate for gas-liquid chromatographic analysis (GLC).

Alachlor, carbofuran, atrazine, and malathion were analyzed with an alkali flame ionization detector on a Varian 2100 gas chromatograph.

Instrument parameters and operating conditions were:

Column:	6 ft glass, packed with 3 percent OV–17 on 100–120-mesh Gas-Chrom Q, internal diameter 2 mm	
Temperatures:	column	210°C
	injection port	235°C
	detector	240°C
Carrier gas:	nitrogen flowing at 15 ml/minute	

Organochlorine pesticides and PCBs were measured by Ni^{63} electron-capture gas chromatography under the above conditions with one exception. The column was packed with a mixture of 3 percent OV–210 and 1.5 percent OV–17 on 100–120-mesh Gas-Chrom Q.

For 2,4,5-T analysis, a methyl ester derivative was prepared for GLC with 10 percent boron trichloride in methanol. GLC injection volumes were 1–10 μl. One milliliter final solution for GLC injection represented 1000 ml original water sample and 100 grams sediment or fish.

Appropriate recovery experiments were conducted according to the procedures in the *Pesticide Analytical Manual* (*5*). The results and the detection limits are shown in Table 1. Results reported are not corrected for percent recoveries.

TABLE 1. *Percent recovery and lower limits of detection of pesticides and PCBs from water, and sediment, and fish samples, Black Creek watershed, Allen County, Indiana—1977–78*

Compound	% Recovery [1]		Lower Limit of Detection, ppm
	Water and Sediment	Fish	
2,4,5–T	95	90	0.0002
PCBs, DDE, dieldrin	98	98	0.0002
Malathion	97.5	92	0.001
Atrazine, alachlor, carbofuran	95	90	0.1

[1] % Recovery = [amount of compound analyzed/(amount of compound added — amount occurring in sample)] × 100

Results and Discussion

No organochlorine pesticide residues were detected in water or sediment samples (Table 2), reflecting both the current low use of the compounds within the watershed and a two-week period without storm runoff prior to sampling. Despite the absence of pesticide residues in the abiotic environment, low levels of dieldrin (mean 0.023 ± 0.0048 μg/g (SE), $n = 18$) and DDE (mean 0.016 ± 0.0017 μg/g (SE), $n = 18$) were found in all fish samples. Similar DDE concentrations have been reported in small-stream fishes from other watersheds where DDE was rarely detected in sediments or water (*4*). The source of the pesticide residues in the *S. atromaculatus* specimens collected in Black Creek cannot be ascertained at present. The absence of organochlorine residues in sediments plus evidence of seasonal upstream movement of the older individuals of this species (*2*) support the hypothesis that the pesticide residues were assimilated in the Maumee River. However, the young age of the individuals collected and the species' decided preference for small-stream habitats suggests that the fishes might occasionally be exposed to organochlorine pesticide residues in Black Creek during periods of storm runoff.

TABLE 2. *Pesticide and PCB concentrations in the Black Creek aquatic environment, Allen County, Indiana—1977–78* [1]

Compound	No. of Samples Collected	No. of Samples Containing Compound	Concentrations [2]		
			Maximum	Minimum	Mean
WATER					
2,4,5–T	8	8	0.008	0.001	0.003
PCB					
Aroclor 1254	7	2	0.0004	0.0002	0.0003
Aroclor 1242	7	0			
FISH					
Dieldrin	18	18	0.086	0.004	0.023
DDE	18	18	0.031	0.007	0.016
PCB					
Aroclor 1254	18	13	0.265	0.070	0.102
Aroclor 1242	18	1	0.140		

[1] Atrazine, alachlor, carbofuran, and malathion were not detected. No compounds were detected in any sediment samples.
[2] Water, mg/liter; fish, μg/g wet weight.

PCBs were detected in two of seven water samples at 0.4 μg/liter and 0.2 μg/liter. Atmospheric inputs and/or sewage outfall sources could account for the presence of PCBs in water (*1*). Sediments did not contain PCBs. Of the fish sampled, 72 percent contained PCBs at a mean concentration (0.102 ± 0.0187 μg/g (SE), $n = 18$) five times higher than the organochlorine pesticide residues in fish. These data suggest that PCBs are more prevalent than other organochlorine residues in the aquatic environment of this agricultural drainage. Exposure of the fish to PCBs in the Maumee River is also a possibility.

Atrazine, alachlor, carbofuran, and malathion were not detected in any samples. Considering the rapid breakdown of these compounds and the low flow conditions that existed for 15 days prior to sampling, these results are not unexpected.

In 1977, the herbicide 2,4,5-T was detected in two water samples at concentrations less than 3 μg/liter but was not present in sediment or fish samples. In 1978, a fish kill was noted three days after application of 2,4,5-T along stream banks. Surface water samples taken seven days after spraying revealed 2,4,5-T concentrations ranging from 0.2 to 7.7 μg/liter. Based on field observations, authors predict frequent occurrence of 2,4,5-T in small streams during summer low-flow periods. Widespread use of the herbicide to kill woody vegetation adjacent to streams, and the common methods of application, make contact with surface water inevitable.

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NOTIFICATION OF CONFERENCE CANCELLATION

The U.S. EPA International Conference on the *Application of Appropriate Technology to Chemical Dose and Chemical Residue Monitoring* scheduled for May 28–30, 1980 at the Sheraton International Conference Center in Reston, Virginia has been cancelled. All expressed interest is appreciated.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
ALDRIN	Hexachlorohexahydro-*endo*, *exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1242	PCB, approximately 42% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
ATRAZINE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
CARBOFURAN	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT); *p,p′*-DDE: 1,1-Dichloro-2,2-bis(p-chlorophenyl) ethylene; *o,p′*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p′*-DDT): ǎ-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p′*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo*-*exo*-5,8-dimethanonaphthalene
ENDRIN	Hexachloroepoxyoctahydro-*endo*,*endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
MALATHION	*O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1-*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene
PPBs (Polybrominated Biphenyls)	Mixtures of brominated biphenyl compounds having various percentages of bromine
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.

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